Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Carbon dioxide and water adsorption on the low-index surfaces of TiC, VC, ZrC and NbC: A DFT study

Matthew G. Quesne†, Alberto Roldan†, Nora H. de Leeuw† and C. Richard A. Catlow†

†School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff CF10 3AT, UK.

Table S1. Geometry scans for CO_2 on four low-index surfaces of NbC. The distance between the surfaces and adsorbate (Cslab) are given in Å; whilst the energies of the total (E_{TOT}) and relative values are given in eV.

NbC{001}				NbC{011}			
CSlab	E_{TOT}	ΔE^a	ΔE^b	CSlab	E_{TOT}	ΔE^a	ΔE^b
3.13	-1018.49	-0.20	0.00	2.31	-985.89	-0.29	0.00
2.90	-1018.49	-0.21	-0.01	2.13	-985.89	-0.28	0.01
2.66	-1018.43	-0.14	0.06	1.96	-985.82	-0.22	0.07
2.43	-1018.32	-0.04	0.17	1.78	-985.73	-0.13	0.16
2.19	-1018.25	0.03	0.23	1.61	-985.76	-0.16	0.13
1.96	-1018.49	-0.21	0.00	1.44	-985.83	-0.23	0.06
NbC{111}C				NbC{111}M			
CSlab	E_{TOT}	ΔE^a	ΔE^b	CSlab	E_{TOT}	ΔE^a	ΔE^b
2.95	-956.01	-0.21	0.00	1.55	-954.47	-1.98	0.00
2.81	-955.99	-0.20	0.02	1.72	-954.21	-1.73	0.25
2.64	-955.95	-0.16	0.05	2.08	-952.97	-0.49	1.49
2.46	-955.87	-0.08	0.14				
2.28	-955.73	0.07	0.28				
2.10	-955.53	0.26	0.48				
1.93	-955.23	0.56	0.78				
1.75	-955.56	0.23	0.45				
1.57	-956.09	-0.30	-0.09				

[a]Energy relative to separate slab and CO_2. [b]Energies relative to physically adsorbed state

Table S2. Geometry scans for CO_2 on four low-index surfaces of ZrC. The distance between the surfaces and adsorbate (Cslab) are given in Å; whilst the energies of the total (E_{TOT}) and relative values are given in eV.

ZrC{001}				ZrC{011}			
CSlab	E_{TOT}	ΔE^a	ΔE^b	CSlab	E_{TOT}	ΔE^a	ΔE^b
2.92	-959.73	-0.27	0.00	2.56	-922.35	-0.23	0.00
2.68	-959.70	-0.24	0.03	2.36	-922.34	-0.22	0.00
2.44	-959.66	-0.20	0.07	2.16	-922.34	-0.22	0.01
2.20	-959.62	-0.16	0.11	1.96	-922.35	-0.23	0.00
1.95	-959.71	-0.25	0.02	1.76	-922.39	-0.27	-0.04
1.71	-960.15	-0.69	-0.43	1.56	-922.46	-0.34	-0.12
				1.36	-922.77	-0.65	-0.42
ZrC{111}C				ZrC{111}M			
CSlab	E_{TOT}	ΔE^a	ΔE^b	CSlab	E_{TOT}	ΔE^a	ΔE^b
3.07	-879.22	-0.25	0.00	1.40	-883.32	-3.32	0.00
2.67	-879.13	-0.16	0.09	1.58	-883.17	-3.16	0.16
2.49	-879.04	-0.08	0.17	1.94	-882.07	-2.06	1.25
2.31	-879.06	-0.09	0.16	2.12	-882.12	-2.12	1.20
2.12	-878.95	0.01	0.27				
1.94	-894.31	-15.34	-15.09				
1.76	-894.33	-15.37	-15.12				
1.58	-894.32	-15.36	-15.11				
1.39	-894.33	-15.36	-15.11				

[a]Energy relative to separate slab and CO_2. [b]Energies relative to physically adsorbed state

Table S3. Geometry scans for CO_2 on four low-index surfaces of TiC. The distance between the surfaces and adsorbate (Cslab) are given in Å; whilst the energies of the total (E_{TOT}) and relative values are given in eV.

TiC{001}				TiC{011}			
CSlab	E_{TOT}	ΔE^a	ΔE^b	CSlab	E_{TOT}	ΔE^a	ΔE^b
3.13	-931.20	-0.26	0.00	0.93	-897.91	-3.45	0.00
2.90	-931.16	-0.23	0.03	1.13	-897.79	-3.33	0.12
2.67	-931.14	-0.21	0.05	1.32	-897.52	-3.06	0.39
2.44	-931.08	-0.14	0.11	1.51	-897.19	-2.73	0.72
2.21	-930.98	-0.04	0.22	1.70	-896.80	-2.34	1.11
1.98	-930.91	0.03	0.29	1.90	-896.19	-1.73	1.72
1.74	-931.06	-0.13	0.13	2.09	-895.57	-1.11	2.34
				2.28	-894.95	-0.49	2.96
				2.48	-894.64	-0.18	3.27
				2.67	-894.54	-0.08	3.37
				2.86	-894.63	-0.17	3.28
				3.05	-894.78	-0.32	3.14
				3.25	-894.83	-0.37	3.08
				3.44	-894.78	-0.32	3.13
				3.63	-894.70	-0.24	3.22
				3.82	-894.58	-0.12	3.34
				4.02	-894.61	-0.16	3.30

[a]Energy relative to separate slab and CO_2. [b]Energies relative to physically adsorbed state

Table S4. Geometry scans for CO_2 on four low-index surfaces of VC. The distance between the surfaces and adsorbate (Cslab) are given in Å; whilst the energies of the total (E_{TOT}) and relative values are given in eV.

VC{001}				VC{011}			
CSlab	E_{TOT}	ΔE^a	ΔE^b	CSlab	E_{TOT}	ΔE^a	ΔE^b
2.90	-949.52	-0.32	0.00	3.10	-919.06	-0.22	0.00
2.67	-949.50	-0.29	0.02	2.92	-919.05	-0.21	0.01
2.45	-949.44	-0.24	0.08	2.73	-918.99	-0.15	0.07
2.22	-949.40	-0.20	0.12	2.54	-918.85	-0.01	0.21
2.00	-949.26	-0.05	0.26	2.35	-918.87	-0.03	0.19
1.77	-949.27	-0.06	0.25	2.16	-918.85	-0.01	0.21
1.55	-949.47	-0.26	0.06	1.97	-918.87	-0.02	0.19
				1.79	-918.99	-0.15	0.07
				1.60	-919.02	-0.18	0.04

[a]Energy relative to separate slab and CO_2. [b]Energies relative to physically adsorbed state

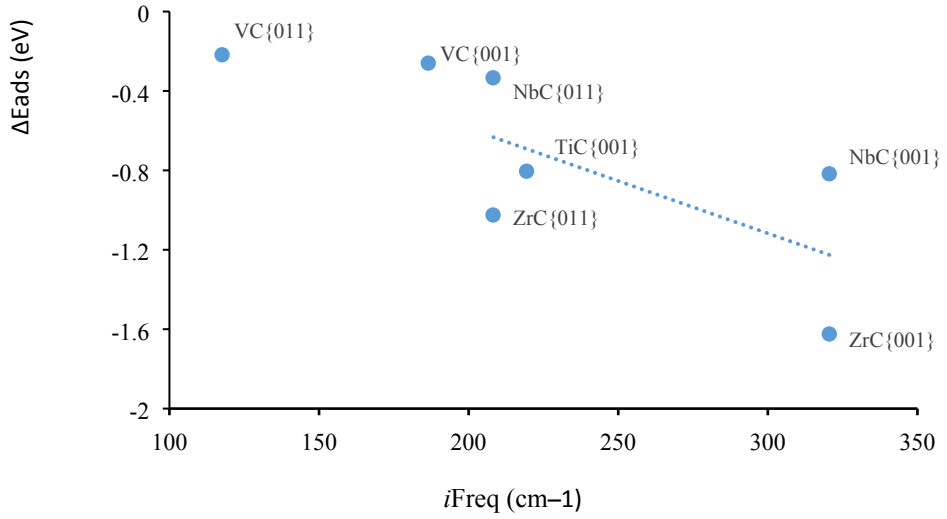

Figure S1. Negative correlation between chemical adsorption energy and the imaginary frequency for the CO_2 reduction transition state.

Table S5. Changes in workfunction (φ), absorption energy (ΔE) and the grouped adsorbate Bader chrges (β) for CO_2 adsorption. The physically and chemically adsorbed states are indicated by subscript phys and chem, respectively. All energies are given in eV.

	Φ_{phys}	Φ_{chem}	ΔE_{phys}	ΔE_{chem}	β_{phys}	β_{chem}
TiC{001}	2.81	~	-0.08	-0.53	0.02	~
TiC{011}	~	2.80	~	-3.43	~	0.00
TiC{111}C	5.73	5.12	~	~	0.00	-0.19
TiC{111}M	~	5.14	~	-0.98	~	0.08
VC{001}	3.31	3.36	-0.17	-0.57	0.02	0.03
VC{011}	~	3.42	-0.45	~	~	0.67
VC{111}C	4.55	~	~	~	0.00	~
VC{111}M	~	4.85	~	-0.96	~	0.16
ZrC{001}	2.87	2.96	~	-0.59	0.02	0.00
ZrC{011}	~	4.08	~	-0.70	~	0.06
ZrC{111}C	~	~	-0.43	~	~	~
ZrC{111}M	~	4.91	~	-1.05	~	0.08
NbC{001}	~	3.13	-0.18	~	~	0.07
NbC{011}	~	2.59	~	-0.80	~	0.02
NbC{111}C	5.00	~	-0.31	-1.01	0.00	~
NbC{111}M	~	5.08	~	-0.87	~	0.11

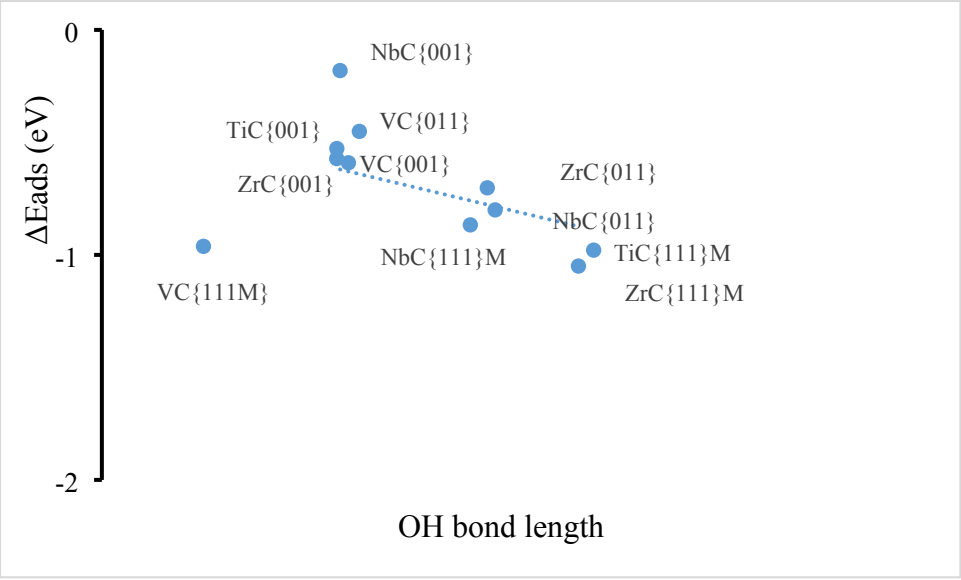

Figure S2. Correlation between chemical adsorption energy and the H_2O bond length of H_2O reduction transition state.

Table S6. Geometry scans for H_2O on the {001} surfaces of TiC and VC, which have been preloaded with CO_2. The distance between the surfaces and adsorbate (Cslab) are given in Å; whilst the energies of the total (E_{TOT}) and relative values are given in eV.

TiC{001}				VC{001}			
CSlab	E_{TOT}	ΔE^a	ΔE^b	CSlab	E_{TOT}	ΔE^a	ΔE^b
4.68	-946.31	-0.01	-0.32	4.86	-964.07	-0.37	-0.33
4.45	-946.32	-0.01	-0.32	4.64	-964.07	-0.37	-0.33
4.22	-946.32	-0.02	-0.33	4.41	-964.08	-0.38	-0.34
3.98	-946.33	-0.03	-0.34	4.19	-964.08	-0.38	-0.34
3.75	-946.35	-0.04	-0.36	3.96	-964.09	-0.39	-0.35
3.52	-946.37	-0.06	-0.37	3.74	-964.10	-0.40	-0.36
3.29	-946.38	-0.08	-0.39	3.51	-964.11	-0.41	-0.37
3.06	-946.38	-0.07	-0.38	3.29	-964.12	-0.42	-0.38
2.83	-946.32	-0.02	-0.33	3.06	-964.14	-0.44	-0.40
2.60	-946.18	0.12	-0.19	2.84	-964.14	-0.44	-0.40
2.37	-945.91	0.39	0.08	2.61	-964.11	-0.41	-0.37
2.14	-946.46	-0.15	-0.46	2.39	-964.03	-0.33	-0.28
				2.16	-963.87	-0.17	-0.13
				1.94	-963.66	0.04	0.09
				1.71	-964.67	-0.97	-0.93

[a]Energy relative to separate slab and CO_2. [b]Energies relative to physically adsorbed state

Table S7. Geometry scans for H_2O on the {001} surfaces of NbC and ZrC, which have been preloaded with CO_2. The distance between the surfaces and adsorbate (Cslab) are given in Å; whilst the energies of the total (E_{TOT}) and relative values are given in eV.

NbC{001}				ZrC{001}			
CSlab	E_{TOT}	ΔE^a	ΔE^b	CSlab	E_{TOT}	ΔE^a	ΔE^b
4.52	-1033.65	0.00	-0.35	4.31	-975.63	0.00	-0.32
4.29	-1033.66	-0.01	-0.35	4.07	-975.63	0.00	-0.32
4.05	-1033.66	-0.01	-0.35	3.83	-975.64	-0.01	-0.33
3.82	-1033.67	-0.02	-0.36	3.59	-975.65	-0.02	-0.35
3.58	-1033.68	-0.03	-0.37	3.34	-975.68	-0.05	-0.38
3.35	-1033.68	-0.03	-0.38	3.10	-975.71	-0.08	-0.41
3.11	-1033.67	-0.02	-0.37	2.86	-975.72	-0.09	-0.42
2.88	-1033.63	0.02	-0.32	2.62	-975.69	-0.06	-0.39
2.65	-1033.63	0.02	-0.32	2.37	-975.59	0.04	-0.29
2.41	-1033.51	0.14	-0.20	2.13	-975.39	0.24	-0.09
2.18	-1033.27	0.38	0.03	1.89	-975.94	-0.31	-0.64
1.94	-1034.14	-0.49	-0.83				

[a]Energy relative to separate slab and CO_2. [b]Energies relative to physically adsorbed state